Quarterly Progress Report

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FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL AND OPTICAL PROPERTIES OF GALLIUM ARSENIDE

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PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

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The purpose of this project is to develop power rectifiers and solar batteries which will operate at temperatures up to 500°C. During this quarter, further results have been obtained in the melting temperatures of GaP-metal systems (to aid in the formation of ohmic contacts) and the growth of GaP by vertical liquid epitaxy has been continued. In the latter case, a new system has been designed, built, and tested. It is felt that this system offers distinct advantages over previous equipment used at Stanford.

Melting Temperature of GaP-Metal Systems

To determine potentially useful metals for ohmic contacts to GaP, the melting temperature of GaP-Au, GaP-Al, GaP-Ag, and GaP-Ni were measured. In each case, the metal was evaporated on a GaP (111) wafer which was tellurium doped to a carrier concentration of 2×10^{17} cm^{-3}. The sample was then heated on a molybdenum strip-heater in a forming gas atmosphere and the alloying process was observed under a microscope. The temperature of the sample was measured by attaching to the strip-heater a thermocopule which had previously been calibrated by the known eutectic temperatures of Si-Au, Si-Al, and Si-Ag systems. The measured melting temperatures are shown in Table I. All measurements were repeated at least once with nearly identical results.

In the cases of GaP-Au and GaP-Al, the melt wetted the GaP surface satisfactorily. However, due to the nature of the experiment, the samples were held at temperatures at or above the alloying temperatures for a period of time. During this time, the metal formed into a smooth hill-like structure on the GaP. For the cases of GaP-Au and GaP-Ni, poorer wetting characteristics were found. Upon heating, the previously mentioned bunching or clustering became more severe with small islands of metal formed on the otherwise uncovered GaP surface. Under all circumstances, the recrystallization did not produce the fine-grained structure which is characteristic of a eutectic but rather yielded a layer with a smooth metallic appearance. Possibly because of the nonuniform alloying on the surface as evidenced by the clustering, none of these metal systems produced reliable ohmic contacts. However, the present plans are to use an n-type dopant with the metal system, e.g., the Ni-Ge mixtures previously described in the last quarterly report, to achieve repeatable results. Therefore, these mixtures will next be tried on a strip-heater where the alloying process can be observed closely under the microscope. Finally, information so obtained will be used to alloy the metal-dopant mixture in a hydrogen-atmosphere furnace where the times and temperatures are closely controllable.

Vertical Liquid Epitaxy

As described in the last quarterly report, work has continued on the growth of thin high purity n-type layers of GaP by vertical liquid epitaxy. The goal of this aspect of the work is to be able to grow consistently, layers 10 to 20 microns in thickness of a carrier concentration in the low 10^{15} cm^{-3} region upon n^{+} substrates. The initial efforts this quarter used essentially the same system as had been developed last year (Quarterly Progress Report for the period October 1 to December 13, 1968). That system had incorporated a new quartz seed holder of our design which eliminated a source of possible contamination. As a result, considerably better material than previously available was grown. However, our present work has been unable to repeat the results. Four consecutive attempts were made with the resultant carrier concentrations being from 2×10^{17} cm^{-3} to 1×10^{18} cm^{-3}. The problem was traced to a substantial melt-back of the seed material with subsequent regrowth. The suspected reason for the melt-back is an incomplete saturation of the melt at the growth temperature due to the loss of phosphorus during the saturation procedure. This problem has always existed in our growth attempts due to the nature of the process.

Specifically, in the process, saturation is accomplished by placing source material (here high purity polycrystalline GaP) in the seed holder, raising the temperature of the gallium melt to near the growth temperature, immersing the source material for an extended time (approximately 4 hours), withdrawing the source material, and cooling the melt to room temperature. The system is then opened and the source material is replaced by the epitaxial seed material. The melt is now reheated to the growth temperature, the seed material immersed, and the melt cooled until sufficient growth has been accomplished. The seed is then withdrawn, the system is cooled to room temperature, and the seed with the growth is removed. The phosphorus loss occurs during the second heating of the melt. In fact, common procedure has been to saturate at a temperature of 5° to $15^{\circ}C$ above the desired growth temperature to compensate for the loss. However, the method is unreliable. Therefore we have designed a new system which eliminates the need for the second heating of the melt.

In the new system, two seed holders have been incorporated such that immediately following saturation and without cooling to room temperature, growth may be started. Previous attempts to design such a system had been unsuccessful due either to construction or alignment difficulties. The new design uses a coaxial principle to overcome these problems. The essential features are given in Fig. 1. Each seed holder, in this case two are used, may be rotated individually into position in the center of the reaction tube and lowered into the melt. When not in use, a holder remains in the system near one of the side walls. This approach differs from earlier ones in that coaxial tubing is used rather than individual rods being placed adjacent to each other. As a result, the alignment of the seed holders with respect to each other need only be maintained over the relatively short distance that they are separated instead of a significant fraction of the reaction tube length as would be the case with adjacent rods. Therefore, the main difficulty, namely the seed holders interfering with each other in their movement, is eliminated. Further, the end cap having only one main sleeve rather than two or more is much stronger. The coaxial design also eliminates a possible source of contamination in that the system need not be opened to the atmosphere between saturation and growth.

The design shown in Fig. 1 has been constructed and the first attempt was made to grow material. The results were successful in that saturation of the melt was easily obtained and maintained prior to immersion of the epitaxial seed. No melt-back was observed and a uniform layer approximately 20 microns in thickness was grown. However, the carrier concentration was disappointingly high at 2×10^{17} cm^{-3}. The possible causes for this are not believed to be connected with the new design and will be investigated in the immediate future.

In summary of the crystal growing efforts for this quarter, a new coaxial design has been developed which is believed to offer distinct improvements over former methods. Problem remain to be solved, but the results are encouraging.

Plans for Next Quarter

Work will continue in order to perfect the growing technique with the new coaxial design for the vertical liquid epitaxy system and to produce reliable ohmic contacts through the parallel alloying investigation.

TABLE I

Melting Temperatures of GaP-Metal Systems

System	Melting Temperature
GaP-Au	$520^{\circ} \pm 20^{\circ}C$
GaP-Al	$635^{\circ} \pm 20^{\circ}C$
GaP-Ag	$690^{\circ} \pm 20^{\circ}C$
GaP-Ni	$760^{\circ} \pm 20^{\circ}C$

FIGURE TITLE

Fig. 1 Vertical liquid epitaxy system showing the dual seed holder design.

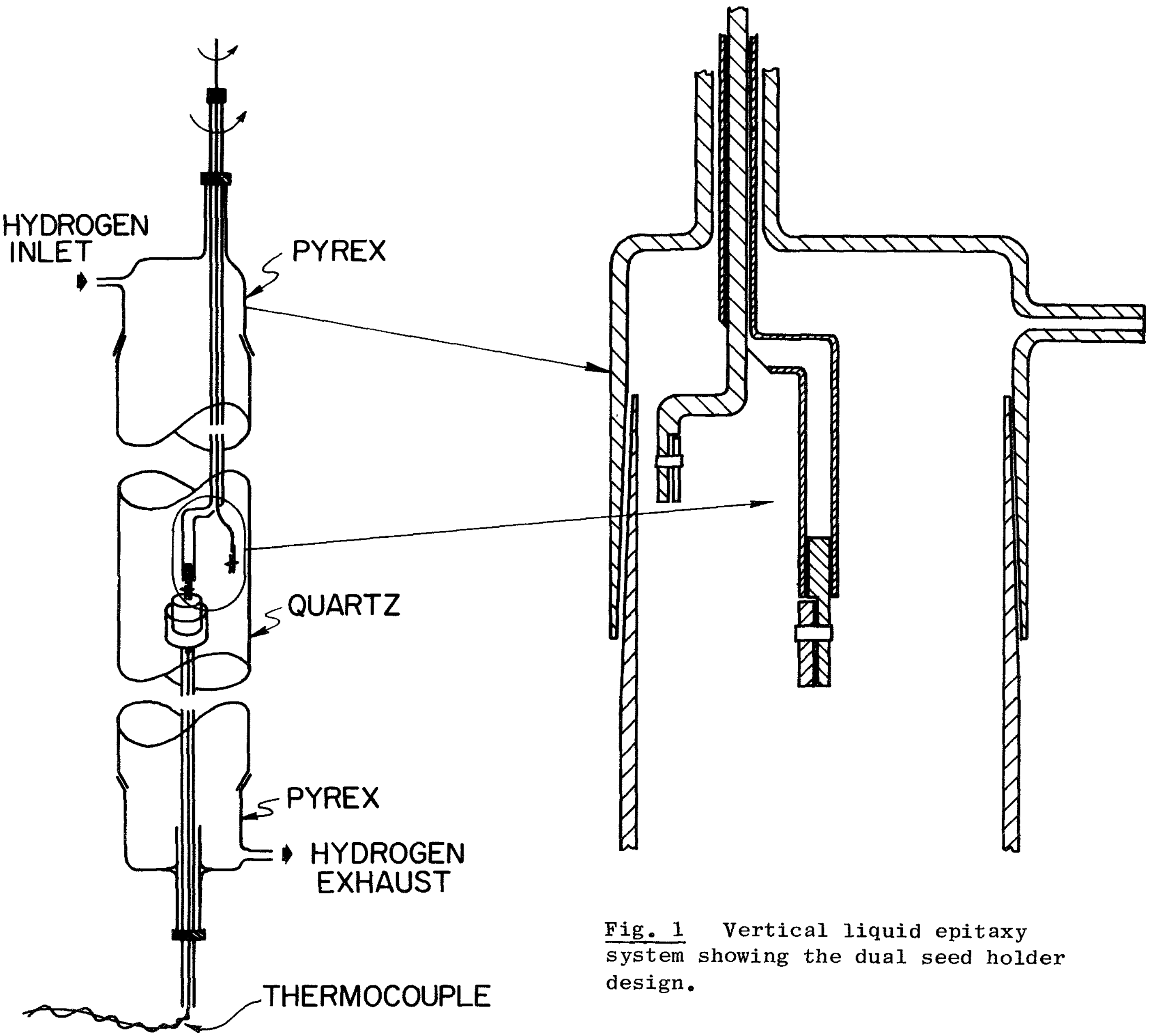

Fig. 1 Vertical liquid epitaxy system showing the dual seed holder design.

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